

**Water-based setting and hardening accelerator for  
hydraulic binders and process for producing it**

**Technical field**

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The invention relates to a setting and hardening accelerator for hydraulic binders according to the preamble of the first claim.

10 The invention likewise relates to a process for producing a setting and hardening accelerator for hydraulic binders according to the preamble of the independent process claim.

**Prior art**

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Many substances which accelerate the setting and hardening of concrete are known. Customarily used substances are, for example, strongly alkaline substances such as alkali metal hydroxides, alkali metal carbonates, alkali metal silicates, alkali metal aluminates and alkaline earth metal chlorides. However, in the case of the strongly alkaline substances, undesirable effects on the processor, e.g. burns, can occur and they reduce the final strength and the durability of the concrete.

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EP 0 076 927 B1 discloses alkaline-free setting accelerators for hydraulic binders, which are said to avoid these disadvantages. To accelerate the setting and hardening of a hydraulic binder such as cement, lime, hydraulic lime, and gypsum, and also mortar and concrete produced therefrom, from 0.5 to 10% by weight, based on the weight of the binder, of an alkali-free setting and hardening accelerator containing aluminum hydroxide is added to the mixture containing said binder.

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Such mortars and concretes are, due to the accelerated setting and hardening, particularly useful as sprayed

mortar and concrete.

EP 0 946 451 B1 discloses setting and hardening accelerators in dissolved form for hydraulic binders, which can be more easily mixed into the concrete when  
5 the concrete is sprayed. Such a setting and hardening accelerator comprises, inter alia, aluminum hydroxide, aluminum salts and organic carboxylic acids. Such known accelerators contain a relatively large amount of aluminum salts and amorphous aluminum  
10 hydroxide, which is very expensive, is required for producing them. To make the production of such accelerators possible, the water for the reaction has to be heated to about 60-70°C. In addition further disadvantages of such setting and hardening  
15 accelerators are a relatively low early strength in the first hours and days and unsatisfactory stability of the solution.

#### **Brief description of the invention**

20 It is an object of the invention to achieve very high early strength combined with very long stability of the accelerator for a water-based setting and hardening accelerator for hydraulic binders of the type mentioned  
25 at the outset.

According to the invention, this is achieved by the features of the first claim.

30 The advantages of the invention are, inter alia, that a high stability, i.e. stabilization of the accelerator solution, is achieved by means of the accelerators of the invention and that high strengths are achieved in the first hours and days.

35 Further advantageous embodiments of the invention are disclosed in the description and the subordinate claims.

### Performance of the invention

- 5 Water-based setting and hardening accelerators according to the invention for hydraulic binders can be produced in various ways, with the molar ratio of aluminum to the organic acid being less than 0.65.
- 10 The term "water-based accelerator" here refers to an accelerator which can be in the form of a solution containing to some extent finely dispersed particles or in the form of a dispersion.
- 15 Such a water-based setting and hardening accelerator according to the invention advantageously comprises (in % by weight):
- from 14.4 to 24.9% of sulfate,
  - from 4 to 9.7% of aluminum (or from 7.6 to 18.3%
  - 20 of  $\text{Al}_2\text{O}_3$ ),
  - 12-30% of organic acid,
  - 0-10% of alkaline earth metal,
  - 0-10% of alkanolamine,
  - 0-5.0% of plasticizer,
  - 25 - 0-20% of stabilizer,
  - and water, with the molar ratio of aluminum to the organic acid being less than 0.65.
- The aluminum content reported as  $\text{Al}_2\text{O}_3$  is preferably less than 14%, particularly preferably less than 13%
- 30 and in particular less than 12%, of  $\text{Al}_2\text{O}_3$ .

- The abovementioned substances are advantageously present as ions in solution but can also be present in complexed form or undissolved form in the accelerator.
- 35 This is the case especially when the accelerator is in the form of a solution containing to some extent finely dispersed particles or in the form of a dispersion.

A water-based setting and hardening accelerator according to the invention for hydraulic binders can be produced, for example, from  $\text{Al}_2(\text{SO}_4)_3$  aluminum sulfate,  $\text{Al}(\text{OH})_3$  aluminum hydroxide and organic acid in aqueous solution, with the molar ratio of aluminum to the organic acid being less than 0.65.

To produce a preferred water-based setting and hardening accelerator according to the invention, use is advantageously made of (in % by weight):

- 30-50% of  $\text{Al}_2(\text{SO}_4)_3$  aluminum sulfate,
- 5-20% of  $\text{Al}(\text{OH})_3$  aluminum hydroxide,
- 12-30% of organic acid,
- 0-10% of alkaline earth metal hydroxide,
- 0-10% of alkaline earth metal oxide,
- 0-10% of alkanolamine,
- 0-5.0% of plasticizer,
- 0-20% of stabilizer,
- balance water, with the molar ratio of aluminum to the organic acid being less than 0.65.

Preferably, an aluminum sulfate containing about 17% of  $\text{Al}_2\text{O}_3$  is used, but it is also possible to use other contents, although the amounts to be added then may have to be adapted accordingly. The aluminum sulfate can also be produced by reaction of aluminum hydroxide with sulfuric acid in the production of the accelerator, with sulfate ions correspondingly being formed in the aqueous solution. In general, aluminum sulfate can be produced by reaction of a basic aluminum compound with sulfuric acid.

Amorphous aluminum hydroxide is advantageously used as aluminum hydroxide. The aluminum hydroxide can also be used in the form of aluminum hydroxide carbonate, aluminum hydroxysulfate or the like.

As organic acid, preference is given to using a carboxylic acid, particularly preferably formic acid, but it is also possible to use other organic acids

having an equivalent effect, e.g. acetic acid. In general, it is possible to use all monoprotic or multiprotic carboxylic acids.

Since sulfate is used in the accelerator, magnesium hydroxide  $Mg(OH)_2$  is preferably used as alkaline earth metal hydroxide. The same applies to the alkaline earth metal oxide, so that magnesium oxide  $MgO$  is then preferably used.

Diethanolamine DEA is advantageously used as alkanolamine.

As plasticizer, use is advantageously made of polycarboxylates, particularly advantageously Sika ViscoCrete®.

Silica sol is advantageously used as stabilizer.

To produce particularly advantageous setting and hardening accelerators, use is made essentially of (in % by weight):

- from 30-50% of  $Al_2(SO_4)_3$  aluminum sulfate, preferably 35-45%, in particular 35-38%, and/or
- 5-20% of  $Al(OH)_3$  aluminum hydroxide, in particular 7-15%, and/or
- 15-23% of organic acid and/or
- 1-10% of alkaline earth metal hydroxide, in particular 2-6%, and/or
- 1-5% of alkaline earth metal oxide and/or
- 1-3% of alkanolamine and/or
- 0.1-3.0% of plasticizer, in particular from 0.1 to 1.0%, and/or
- 0-10% of stabilizer,
- balance water, with the molar ratio of aluminum to the organic acid being less than 0.65, preferably less than 0.60, particularly preferably less than 0.55 and in particular less than 0.50.

The molar ratio of aluminum to the organic acid is preferably in the range from 0.38 to 0.65, particularly preferably in the range from 0.38 to 0.60, in

particular from 0.50 to 0.60. Below a value of 0.38, the pH becomes relatively low and a very high proportion of acid has to be used; in addition, the stability is sometimes no longer ensured.

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Compared to conventional setting accelerators, the amount of the aluminum sulfate used for producing the accelerator and, in particular, the amount of aluminum hydroxide are reduced by up to 10% and 38%, respectively. In the production of the accelerator, preference is given to using up to 10% of magnesium hydroxide and/or a corresponding amount of magnesium oxide. The pure Mg amount based on the total amount of accelerator is from 0 to 4.2%, preferably from 0.8 to 2.9%, particularly preferably from 1.3 to 2.1%.

The ratio of aluminum to the organic acid is set to a value of less than 0.65, preferably less than 0.60, as a result of the increased organic acid content compared to known accelerators and the pH is set to 3-4 by means of up to 5% of alkanolamine.

The reduction by up to 25% in the amount of the aluminum used in the production of the accelerator improves the sulfate resistance. This is an advantage over conventional accelerators in the case of which the sulfate resistance is drastically worsened by the accelerator. The reduction in the sulfate resistance due to introduction of aluminum is caused especially by the aluminate phases having a particular affinity for sulfate. The additional aluminum increases the proportion of aluminate phases in the concrete, which then in the event of external sulfate acting on the cured concrete cause a not insignificant crystallization pressure due to ettringite formation and thus lead to damage. The aluminum content reported as  $\text{Al}_2\text{O}_3$  is therefore preferably kept below 14%, particularly preferably below 13% and in particular below 12%, of

$\text{Al}_2\text{O}_3$ .

If magnesium hydroxide and/or oxide is used in the production of the accelerator, the temperature of the mixture rises as a result of the vigorous reaction of the magnesium hydroxide and/or oxide with the organic acid to such an extent that the water for these mixes does not have to be heated. The further components are then added to this heated mixture. However, the components can also be added in any other order. This simplifies the process and less energy is required. An additional advantage of the use of magnesium is the significantly increased storage stability of the accelerators brought about by the magnesium ions. Even at a content of 1% by weight of magnesium hydroxide in the production of the accelerator, good storage stability is achieved. At higher contents, the storage stability is at least four months. The use of magnesium hydroxide and/or oxide also enables the accelerator to be produced significantly more cheaply since expensive aluminum hydroxide can be replaced. In addition, the stability of the accelerators is positively influenced by the reduced amount of aluminum. The sulfate resistance is also increased by the reduced amount of aluminum.

The development of the compressive strength of the sprayed concrete in the first hours and days is also influenced very positively and is better than in the case of conventional accelerators.

### Examples

A number of samples of accelerators according to the invention were produced in accordance with the values indicated in Table 1, using aluminum sulfate containing 17% of  $\text{Al}_2\text{O}_3$  and amorphous aluminum hydroxide, and compared with a comparative example B1 of a conven-

tional accelerator.

Example	H <sub>2</sub> O	Al(OH) <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (17% of Al <sub>2</sub> O <sub>3</sub> )	Mg(OH) <sub>2</sub>	HCOOH (85%)	DEA
A1	17.20	15.00	41.00	1.30	22.50	3.00
A2	22.50	10.00	41.00	5.00	18.50	3.00
A3	25.00	13.50	37.00	1.30	20.50	2.70
A4	28.00	10.00	37.00	4.50	17.50	3.00
A5	19.8	15.0	41.2	0.0	22.5	3.0
A6	26	10	37	4.5	19.5	3
A7	20.5	10	37	4.5	25	3
A8	15.5	10	37	4.5	30	3
B1 (L53AF)	23	16	41	0	10	0

5 Table 1: Sample composition in % by weight

To produce the accelerators A1 to A4 and A6 to A8, water is initially provided in unheated form. The magnesium hydroxide is slurried therein and formic acid  
 10 is added, resulting in a large increase in the temperature. The aluminum hydroxide, the aluminum sulfate and the diethanolamine DEA are then added. The total mixture is then stirred until the reaction has abated and the temperature has dropped to about 40°C  
 15 after about one hour. This results in a solution which, depending on the composition, can also contain finely dispersed particles.

To produce the accelerator A5 without magnesium  
 20 hydroxide or oxide, water was initially charged in preheated form. The formic acid is added to the water and the aluminum hydroxide is then added. The aluminum sulfate and the diethanolamine are then added. The total mixture is stirred until the reaction has abated.



Table 2 shows the molar ratios of aluminum to sulfate and of aluminum to the organic acid, here formic acid, of the samples measured. The values of the molar ratios of aluminum to the organic acid are below 0.67, preferably below 0.60. The aluminum content is also given for the various examples.

Example	Al/sulfate	Al/organic acid	% of Al	% of Al <sub>2</sub> O <sub>3</sub>
A1	2.717	0.658	7.6	14.3
A2	2.256	0.664	6.3	11.9
A3	2.713	0.65	6.8	12.9
A4	2.356	0.662	5.9	11.2
A5	2.710	0.659	7.6	14.4
A6	2.356	0.594	5.9	11.2
A7	2.356	0.463	5.9	11.2
A8	2.356	0.386	5.9	11.2
B1	2.809	1.53	7.9	14.8

Table 2: Molar ratios

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From 0.1 to 10% by weight of the accelerator according to the invention can be added to hydraulic binders. To determine the effectiveness of the accelerator according to the invention of Examples A1 to A6 and of Comparative Example B1, a conventional concrete mixture for use as sprayed concrete was in each case admixed with 6% of the accelerator, based on the content of the hydraulic binder. Portland cement was used as hydraulic binder. The accelerator was in each case introduced in the region of the spray nozzle during processing of the sprayed concrete. After application of sprayed concrete, the strength of the sprayed concrete was determined. For this purpose, drill cores having dimensions of 5 × 5 cm are taken from the concrete. The compressive strength of the drill cores is then determined by means of a hydraulic press.

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It has surprisingly been found that due to the high proportions of organic acid and magnesium and despite the reduced aluminum content, the strengths after from  
5 a few hours to a few days are much better than in the case of conventional accelerators, see Table 3. Although Example A5 displays a relatively high strength after one day, this is at significantly higher aluminum contents than in Examples A6 to A8. Embodiments in  
10 accordance with Examples A4 and A6 to A7 are thus particularly preferred, since the sulfate resistance is also improved by the lower Al content.

Example	A1	A2	A3	A4	A5	A6	A7	A8	B1
Strength (MPL) after one day	18.3	16.3	14.9	16.6	20	20.5	20.6	19.5	12
Strength (MPL) after seven days	47.5	40.4	45.5	48.1	48	48.5	49	47	42.1

Table 3: Strengths in N/mm<sup>2</sup>

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The accelerators of the invention can also be used for hydraulic binders other than cement, for example mixed cements, lime, hydraulic lime, and gypsum, and also mortar and concrete produced therefrom.

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Of course, the invention is not restricted to the examples presented and described.